Polymer Bulletin 10, 487–490 (1983)

Polymer Bulletin

Cationic Polymerization Initiated by Intercalation Compounds of Lewis Acids

Polymerization of Cyclosiloxanes

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ABSTRACT

The results of initial studies showing the high activity of intercalation compounds of Lewis acids ($C_{30}SbCl_5$, $C_{77}FeCl_3$, $C_{64}AlBr_3$) as initiators of the cationic polymerization of cyclosiloxanes are presented. The influence of some reaction conditions on the yield and the molecular mass of the polymers formed is described.

INTRODUCTION

It is known that Lewis acids ($FeCl_3$, $AlCl_3$, $SnCl_4$ etc.) initiate the cationic polymerization of cyclosiloxanes - hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4) without proton donor additives only at temperature above 200°C (ANDRIANOV and JAKUSHKINA, 1960; MOEDRITZER and VAN WAZER, 1964; CHERNYSHEV and YASTREBOV, 1969). Even in the presence of such cocatalysts and in polar solvents the polymerization rate at 25 - 30°C is low and the polymer yields rarely exceed 50 % (KENDRICK, 1965).

It is known that the interaction between graphite and Lewis acids yields intercalation compounds (IC) of the following type:

$$C_x(M^{n+}Hal_n)_y$$

where M is Fe, Al, Sb etc., Hal is Cl, Br etc., and x,y are the carbon atoms from the graphite layers and the intercalated molecules of the Lewis acid. These IC posses an ionic character because of the electron transfer from the graphite to the acid accompaning the intercalation process (PENTENRIEDER and BOEHM, 1982). The resulting compounds might be represented by the following formulae:

$$[graphite]^+[Fe^{2+}Cl_2.Cl^-].xFeCl_3$$

$$[graphite]^+[SbCl_6]^-.ySbCl_5.zSbCl_3$$

If we consider these IC to be structural analogues of the complexes of the Lewis acids with proton donors of the type

$$H^+[M^{n+}Hal_n.Y]^-$$

it can be expected that the graphite layers would act like the proton from the described complex. It may be assumed that IC would have high initiation ability. However, data for their use as initiators of the cationic polymerization are lacking in the literature up to now.

Our preliminary investigations have shown that in the presence of solvents like chloroform or dichloroethane D_3 and D_4 polymerize under the action of IC of $FeCl_3$ and $SbCl_5$, but the polymerization mixtures are coloured by the extracted into the homogeneous phase Lewis acid. In n-heptane solution the polymerization of D_3 and D_4 is extremely slow - at 20°C after 48 hours the conversion of D_4 does not exceed 26 % (monomer concentration 0,8 mol/l). This is probably due to the interaction between the initiator and n-heptane. It was proved recently that under the action of IC hexane isomerizes easily even at 20°C (LENORMAND et al., 1982).

The aim of the present work is to check the initiation ability of IC ($C_{30}SbCl_5$, $C_{77}FeCl_3$ and $C_{64}AlBr_3$) in the bulk polymerization of D_3 and D_4. The initiation ability of the pure graphite and Lewis acids were also checked under the same reaction conditions.

EXPERIMENTAL

$C_{30}SbCl_5$ was synthesized from natural Madagascar graphite with particle sizes 100 - 125 µm as described elsewhere (MÉLIN and HÉROLD, 1969).

$C_{77}FeCl_3$ and $C_{64}AlBr_3$ were used as commercially avaible products of Alfa-Ventron Corp.

D_3 and D_4 were dried, distilled and stored in vacuo.

n-Heptane was added to the polymerization mixtures after the termination of the polymerization, the initiator was removed by filtration after which the solvent was evaporated under reduced pressure.

The intrinsic viscosity ($[\eta]$) of the polymerization mixtures was determined in toluene at 25°C.

The molecular mass of the polydimethylsiloxanes formed was calculated by the following formula (CARMICHAEL and WINGER, 1965):

$$[\eta] = 2{,}00.10^{-4}.\bar{M}_v^{0,65}$$

The GPC analyses of the polymerization mixtures were performed at 80°C in toluene on Waters 150C chromatograph equipped with four Ultrastyragel columns the porosities being 10^5, 10^4, 10^3 and 500 Å. Flow rate 1,0 ml/min.

RESULTS AND DISCUSSION

Under the action of $SbCl_5$ and $FeCl_3$ D_3 and D_4 do not polymerize at 70°C and 20°C respectively during a week and longer. A similar behaviour was already described for $FeCl_3$ by other authors (KENDRICK, 1965).

Under the action of pure graphite D_3 and D_4 do not polymerize even at 115°C.

$C_{30}SbCl_5$, $C_{77}FeCl_3$ and $C_{64}AlBr_3$ initiate the polymerization of D_3 (at 70°C) and D_4 (at 20°C). The monomer conversion increases with the polymerization time (Table I). In the case of $C_{86}AlBr_3$ initiated polymerization of D_4 the composition of the polymerization mixtures depends on the time (Figure 1). The molecular mass of the polydimethylsiloxanes formed increases with the increase in the ratio monomer/initiator (Tab-

TABLE I

Time dependence of the quantity and the molecular mass of polydimethylsiloxane formed during the polymerization of D_4 under the action of $C_{30}SbCl_5$. $[C_{30}SbCl_5]$ = 2,5 mole % (against the monomer); 20°C; bulk.

Time (hr)	Yield (%)	$\bar{M}_v$
24	65	22 000
48	72	28 000
96	82	132 000
120	93	14 000

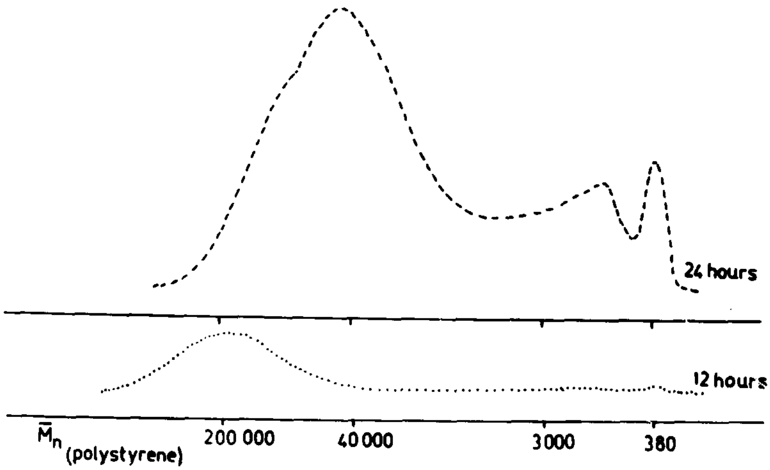

Fig. 1: Gel permeation chromatograms of polydimethylsiloxanes obtained during the $C_{64}AlBr_3$ initiated polymerization of D_4. $[D_4]:[C_{64}AlBr_3]$ = 20; 20°C; bulk.

TABLE II

Influence of the ratio monomer/initiator on the quantity and the molecular mass of polysiloxane formed during the polymerization of D_4 under the action of $C_{77}FeCl_3$. 24 hrs; 20°C; bulk.

$[D_4]:[I]$ (molar)	Yield (%)	$\bar{M}_v$
10	98	249 000
20	80	320 000
40	90	342 000

le II).

The polymerization of D_3 (70°C, 24 hours, $[D_3]:[I] = 20$) initiated by $C_{30}SbCl_5$, $C_{77}FeCl_3$ and $C_{64}AlBr_3$ is faster than the polymerization of D_4 initiated by the same initiators. The yields of rubberlike polymers are 70 - 80 %. These products have limited solubility in toluene.

The increase in temperature causes a great decrease in the quantity of the polymers formed. For example, during the $C_{30}SbCl_5$ initiated polymerization of D_4 at 40°C only oligomers are formed after 24 hours.

The results obtained show that IC are active initiators of the polymerization of cyclosiloxanes. They are much more active than the pure Lewis acids and in some cases - more active than their complexes with proton donor additives. Their usage leads to a formation of polysiloxanes with good yields and relatively high molecular masses at temperatures which are much lower than those described by other authors. It is noteworthy that high yields of high polymers are achieved even by initiators with relatively low contents of intercalated Lewis acid ($C_{77}FeCl_3$ and $C_{64}AlBr_3$).

The influence of the reaction conditions, the type of the intercalated Lewis acid and the size of the monomer ring on the quantity and the molecular mass of the polydimethylsiloxanes formed are under investigation.

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Accepted September 2, 1983

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